

A Comparative Study of HPLC Column Packings for the Separation of Aromatic and Polar Compounds in Fossil Fuel Liquids

Atsushi Matsunaga and Sampo Kusayanagi

Lubricants and Petroleum Products Laboratory, Nippon Mining Co., Ltd.
3-17-35, Niizo-Minami, Toda, Saitama 335, Japan

INTRODUCTION

The upgrading of petroleum residuals, tar sand bitumens, shale oil and coal liquefaction products is a matter of current concern. Polynuclear aromatic hydrocarbons, nitrogen and oxygen compounds are present in relatively large amount in these fuel sources. These compounds can cause serious problems in processing and in the quality of the products. Then, the character and content of these compounds must be known to choose appropriate catalysts and conditions for refining.

Many works on compositional analyses of each liquid have been reported, most of which involve the combination of classical chromatographic separation and spectrometric characterization. Although this approach is undoubtedly most useful, it is very time-consuming to apply to routine analysis for the purpose of process control or product evaluation. Also, the poor separation due to the low efficiency or tailing problems of classical adsorbents causes cross-contamination of fractions in many cases.

Recently, high performance liquid chromatography (HPLC) has been applied to the rapid analysis of petroleum products and alternative fuel sources. Many of the works dealt with the type analysis as a substitute of FIA method (1,2) or so-called SARA method (3,4). Selucky et al. used HPLC on μ -Porasil as a fingerprinting technique of petroleum products (5). Wise et al. employed μ -Bondapak NH_2 column for the separation of polynuclear aromatic hydrocarbons (PAHs) in crude oil (6), while Mourey et al. used microparticulate pyrrolidone column for the analysis of PAHs in shale oil (7). μ -Bondapak NH_2 was also used by Dark et al. for the analysis of anthracene oil (8). It seems apparent that normal phase chromatography is adequate for the class separation of heavy fractions, since the long alkyl chains govern the retention characteristics rather than polar group in the reversed phase mode (6,9). This paper reports a study on normal phase HPLC separations of aromatic and polar compounds using several packing materials.

EXPERIMENTAL

The instrument used was a Varian Aerograph model 5020 Liquid Chromatograph equipped with a UV 254 nm absorbance detector and a ternary solvent programmer. Column packings used are listed in TABLE I. Hexane, methylene chloride and methanol of LC grade were obtained from Wako Chemicals, Tokyo, and used as received.

TABLE I. HPLC COLUMN PACKINGS STUDIED

Packing	Functionality	Particle Diameter (μm)	Column Length (cm)	Column ID (mm)	Theoretical Plate Number	Supplier
Nucleosil NO_2	Nitro-	5	15	4.6	4000	Machery-Nagel Co. (Germany)
Nucleosil NH_2	Amino-				5000	
Nucleosil CN	Cyano-				4900	
Nucleosil SA	Sulfonic Acid-				4600	
Lichrosorb Si-5	Silica	5	25	4.6	7500	E. Merck (Germany)
Lichrosorb Al-5	Alumina				3000	
TSK 111	Styrene-Divinylbenzene Copolymer				3000	
						Toyo Soda (Japan)

RESULTS AND DISCUSSION

MODEL COMPOUND STUDY. TABLE II summarizes the retention data of model aromatic compounds on each stationary phase. The largest capacity factor (k') was obtained using Nucleosil NO_2 column, with the exception of activated alumina. Selectivity (α) for the separation between naphthalene and chrysene is given by the ratio of the capacity factor for both compounds and is also shown in TABLE II. Again, Nucleosil NO_2 gave the largest selectivity. This could be attributed to the large charge-transfer capability of nitrophenyl group with polynuclear aromatic hydrocarbons. Nucleosil NH_2 seems to possess the similar, but weaker, ability, as it gave a better selectivity than silica regardless of the weaker retention for naphthalene. Nucleosil CN and Nucleosil SA columns showed smaller capacity factor than silica. It was difficult to obtain reproducible retention data with alumina/hexane system. Alumina is, however, an important adsorbent since it exhibits the most strong retention for aromatic compounds at activated state and it gives the most distinctive separation between mono- and diaromatics (10). TSK 111 (polystyrene gel) exerts a unique adsorption of aromatic compounds with hexane as eluant, probably due to π - π electron interaction. The difficulty with this system is that retention is very dependent on the size of alkyl substituent and steric exclusion can occur in some cases, that causes the impossibility of separation of substituted compounds by aromatic ring number.

The retention behavior of selected polar compounds are summarized in TABLE III. Pyridine and its benzologues are the known main "basic" nitrogen compounds in fossil liquids. Indole and its derivatives are the typical "nonbasic" nitrogen compounds. Phenols are typical polar components containing oxygen. Carboxylic acids were not studied here as they did not give a clear peak in these LC modes, probably because of association.

Good separation of polar compounds from aromatic hydrocarbons was obtained except for that on TSK 111 as shown in TABLE III. As TSK 111 has no polar group on it, interaction with polar group in sample molecule is weak. The rather strong retention of phenols and indoles will be due to their electrophilic nature. Polar compounds were preferentially retained on the stationary phases other than TSK 111. Gradient elution was carried out for rapid elution of strongly retained molecules. From the data shown in TABLE III, it is considered that polar-polar interactions including hydrogen bonding or acid-base interaction are the predominant separation mechanism, although the effect of alkyl substitution, especially at sterically hindered positions to polar group, is not negligible (e.g. 8-methylquinoline and 2,4-dioctylphenol).

Both Nucleosil NO_2 and Nucleosil CN have neutral functional group and the elution order of compounds on these packings are similar and in accordance with the order of so-called polarity: nonbasic nitrogen compounds < phenols < basic nitrogen compounds. The capacity factors are larger for all compounds with NO_2 column than CN because of its strong polarity. NO_2 showed stronger retention for phenols, with decreasing the selectivity for the resolution between phenols and basic nitrogen compounds (see TABLE III). Nucleosil NH_2 have weakly basic character, and showed strong retention of phenols. Basic and nonbasic nitrogen compounds were not separated each other. The nonbasic nitrogen compounds are weak acids and the interaction with amino group can occur. It is well known that alumina contains a number of strongly basic sites. Then, alumina showed preferential adsorption of nonbasic nitrogen compounds relative to basic compounds. To elute phenols from alumina column, eluant containing a more polar solvent (e.g. methanol) was required. In contrast, Nucleosil SA has strongly acidic functionality and showed strong retention of basic nitrogen compounds. In the case of silica, the elution order approximately depends on sample polarity, although tendency for a preferential adsorption of basic compounds is also observed.

The comparison of selectivities in TABLE III shows that Nucleosil NH_2 and silica give better resolution between phenols and nitrogen compounds and that better separation of nitrogen compounds by types is obtained using silica and Nucleosil SA. The effect of alkyl substitution on separabilities by compound types depend on its position, number and size. From TABLE III, substitution at sterically hindered positions appears to affect most largely. The tendency of this effect seems to be

common to all polar stationary phases studied.

APPLICATION STUDY. Examples of HPLC separations on coal tar and heavy petroleum fractions are described here. FIGURE 1 is the chromatograms on coal tar. With Nucleosil NH_2 column, separation of aromatic compounds by ring number (three-ring aromatics as predominant) and separation between nitrogen compounds and phenols were achieved. Nonbasic nitrogen, phenols and basic nitrogen compounds were separated each other using silica. In the case of alumina, gradient elution using three solvent including methanol was performed to elute phenols. Here again, separation of aromatics by ring number and separation of nitrogen compounds and phenols were obtained. A reversed trace of gradient profile was carried out to regenerate alumina column.

FIGURE 2 demonstrates the HPLC separations on heavy petroleum fractions. Silica, Nucleosil NO_2 , NH_2 and CN columns all gave the similar patterns of chromatograms; with NO_2 and CN columns some overlap were observed between polynuclear aromatics and weakly polar components. Two main peaks in polar region seem to be attributed to basic and nonbasic nitrogen compounds. To examine the HPLC behavior of these components present in the fraction, basic and nonbasic (acidic) compounds were concentrated by chromatography on ion-exchangers (Amberlyst 15 and A29, Rohm and Haas), and collected fractions were injected into HPLC system. Although cross-contamination was observed, particularly in the A29 adsorbate, the attribution of two peaks was proved to be proper. Due to the long and several alkyl substitutions, nitrogen compounds were not retained so strongly as model compounds, while some separability by types still remains. The heavier is the fraction, the more difficult is the separation as shown in FIGURE 2B. FIGURE 2C shows the chromatogram of hydrogenated product of fraction in FIGURE 2A. Broader distribution of nitrogen compounds were observed in FIGURE 2C. These new peaks can be those of the hydrogenated intermediates or products of nitrogen compounds, which possess a variety of basic or nonbasic characters. Separation of aromatic compounds by types was not so clear in petroleum heavy fractions, because of the large alkyl or naphthenic substituents. Some characteristic profiles can be obtained, though, especially with Nucleosil NO_2 . Mono-, di- and polynuclear aromatic fractions were collected by preparative scale chromatography on activated alumina (10) and the well-defined fractions were chromatographed on Nucleosil NO_2 . As shown in FIGURE 3, separability by ring number can be recognized, although clear resolution was not obtained.

REFERENCES

- (1) Suatoni, J.C., Garber, H.R. and Davis, B.E., J. Chromatogr. Sci. 13, 367 (1975).
- (2) Suatoni, J.C. and Garber, H.R., J. Chromatogr. Sci. 14, 546 (1976).
- (3) Suatoni, J.C. and Swab, R.E., J. Chromatogr. Sci. 13, 361 (1975).
- (4) Suatoni, J.C. and Swab, R.E., J. Chromatogr. Sci. 14, 535 (1976).
- (5) Selucky, M.L., Rue, T.C.S. and Strausz, O.P., Fuel 57, 585 (1978).
- (6) Wise, S.A., Chesler, S.N., Hertz, H.S., Hilpert, L.R. and May, W.E., Anal. Chem. 49, 2306 (1977).
- (7) Mourey, T.H., Siggia, S., Uden, P.C. and Crowley, R.J., Anal. Chem. 52, 885 (1980).
- (8) Dark, W.A., McFadden, W.H. and Bradford, D.L., J. Chromatogr. Sci. 15, 454 (1977).
- (9) Schabron, J.F., Hurtubise, R.J. and Silver, F., Anal. Chem. 49, 2253 (1977).
- (10) Matsunaga, A. and Yagi, M., Anal. Chem. 50, 753 (1978).

TABLE II. CAPACITY FACTORS AND SELECTIVITY OF AROMATIC COMPOUNDS^{a)}

Compounds	Nucleosil			Lichrosorb TSK		
	NO ₂	NH ₂	CN	SA	Si-5	111
<u>Capacity factor</u>						
Dodecylbenzene	0.09	0.00	0.06	0.05	0.14	-0.08
Toluene	0.09	0.05	0.06	0.14	0.25	-0.03
Tetraline	0.14	0.05	0.06	0.18	0.33	0.22
Naphthalene	0.68	0.23	0.22	0.23	0.44	0.67
Biphenyl	0.68	0.25	0.29	0.23	0.61	0.67
Fluorene	1.55	0.36				1.03
Anthracene	1.91	0.54	0.53	0.45	0.75	1.67
Fluoranthene	4.64	0.86	0.61			2.11
Pyrene	3.18	0.91		0.55	0.83	2.25
Chrysene	6.27	1.32	0.80	0.82	1.33	3.50
Benzo(e)pyrene	12.18	1.82	1.00		1.69	5.00
Dibenzofuran	1.23	0.36				0.94
Dibenzothiophene	1.72	0.50				1.61
Selectivity(α_1) ^{b)}	9.22	5.74	3.64	3.57	3.02	5.22

a) Carrier: Hexane, 1 ml/min.

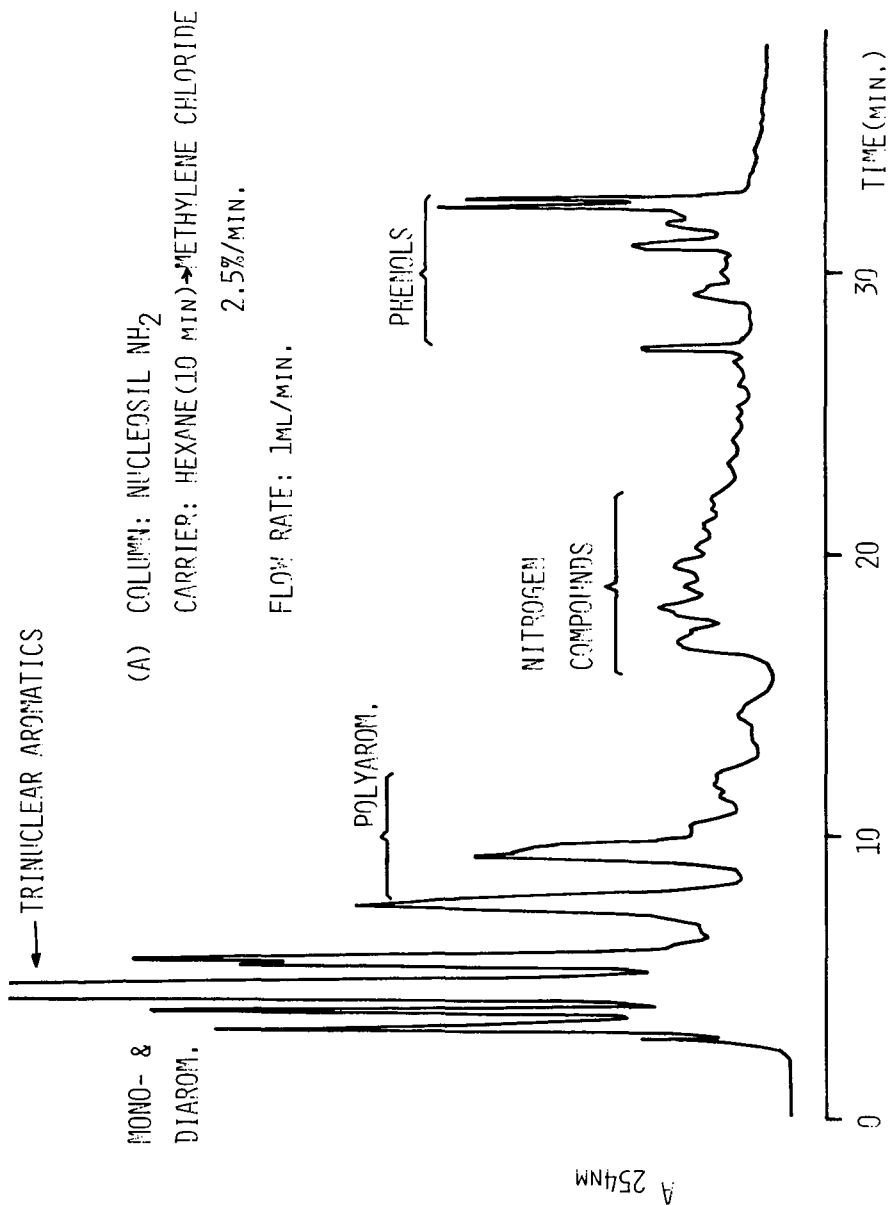
b) $\alpha_1 = k'(\text{chrysene})/k'(\text{naphthalene})$.TABLE III. CAPACITY FACTORS AND SELECTIVITIES OF POLAR COMPOUNDS^{a)}

Compounds	Nucleosil			Lichrosorb			TSK
	NO ₂	NH ₂	CN	SA	Si-5	Al-5	111
<u>Capacity factor</u>							
Indole	9.82	10.73	6.45	8.36	6.89		5.17
2-Methylindole	9.82	10.09	5.82	7.41	6.72		4.53
3-Methylindole	9.27	9.73	5.12	6.68	6.44		3.94
Carbazole	10.73	11.18	7.00	8.27	7.67	6.45	9.08
Pyridine	14.00	11.18	10.29				
Quinoline	13.73	10.82	9.98				1.38
2-Methylquinoline	13.64	10.55					
4-Methylquinoline	14.45		10.29				
7-Methylquinoline	13.91	11.55	9.82				
8-Methylquinoline	8.73	7.64					
2,6-Dimethylquinoline	13.82	11.18	10.29				
Isoquinoline	14.55	12.00	10.37				
Acridine	13.64	10.82	9.04	22.64	16.00	5.55	2.47
Aniline	10.36						
1,2,3,4-Tetrahydroquinoline	9.36	7.18	2.45				
Phenol	13.64	16.27	8.88	13.68	11.00	N.E. ^{e)}	3.94
o-Cresol	11.82	13.55	7.71	10.45			2.81
p-Cresol	14.00		9.27	13.00			3.50
2,5-Xylenol	11.27		7.00				8.39
2,6-Xylenol	8.18		3.16				
3,4-Xylenol	14.00	15.27	8.88				
p-Nonylphenol	12.18	13.73	7.78	11.91	10.11	N.E.	1.69
2,4-Dioctylphenol	6.91		3.16	4.86	6.44		0.47
α -Naphthol	13.55	17.73	9.67				8.39
<u>Selectivity</u>							
α_1 ^{b)}	1.27	1.46	1.27	1.65	1.43	large	2.30
α_2 ^{c)}	1.00	1.50	1.02	1.65	1.45	large	1.60
α_3 ^{d)}	1.27	1.03	1.29	2.74	2.09	1.16	3.68

a) Gradient elution for Nucleosil and Lichrosorb: Hexane(10 min) then to methylene chloride at 2.5%/min. With TSK, isocratic with hexane, 1-ml/min.

b) For phenol & carbazole. c) For phenol & acridine. d) For carbazole & acridine.

e) not eluted.



(A) COLUMN: NUCLEOSIL NH₂

CARRIER: HEXANE (10 MIN) → METHYLENE CHLORIDE

2.5%/MIN.

FLOW RATE: 1ML/MIN.

FIG. 1A

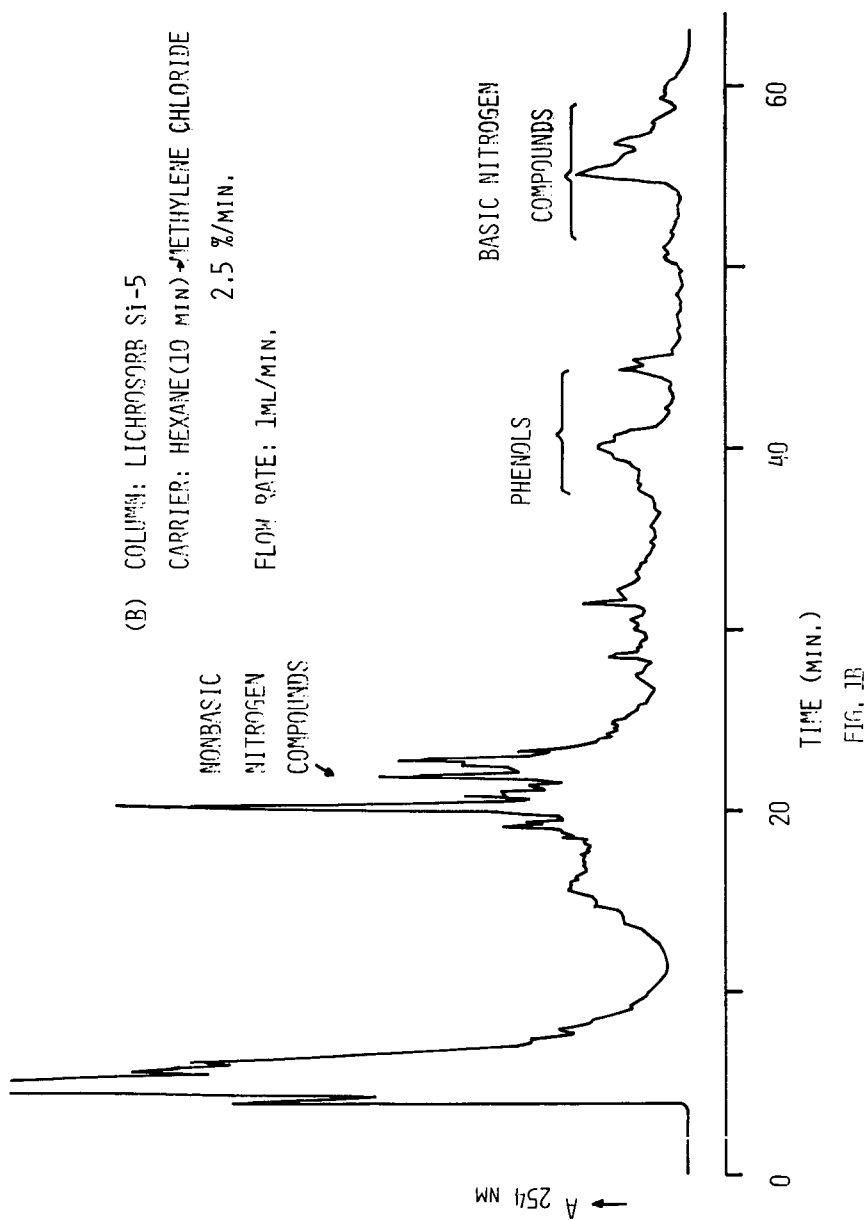


FIG. 1B

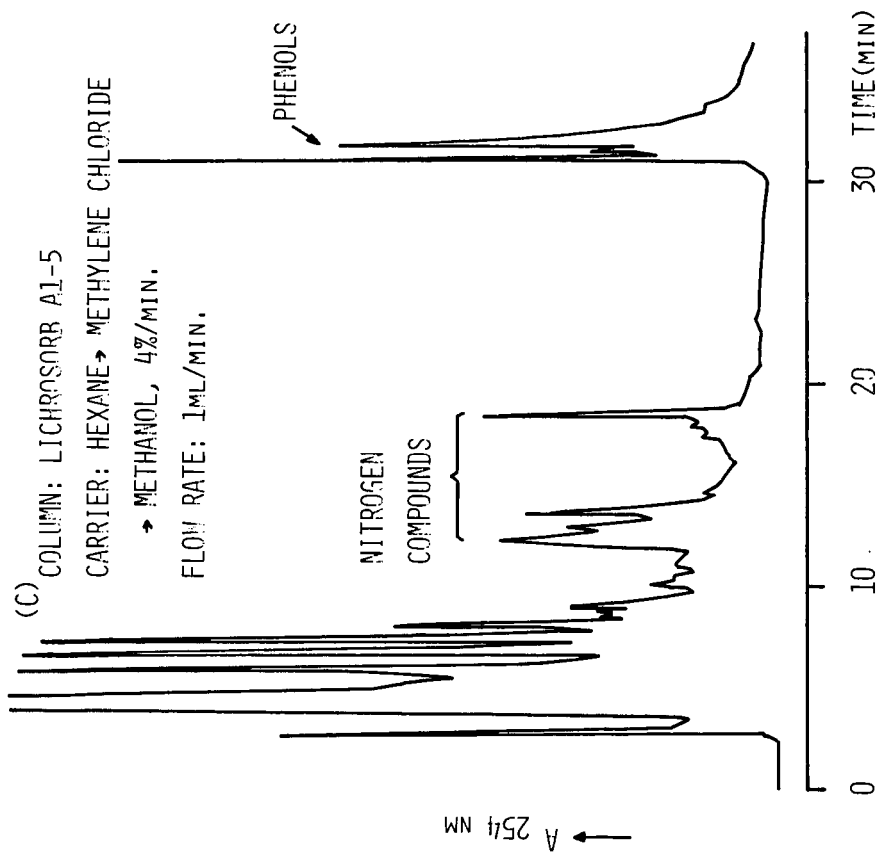


FIGURE 1C CHROMATOGRAMS OF COAL TAR

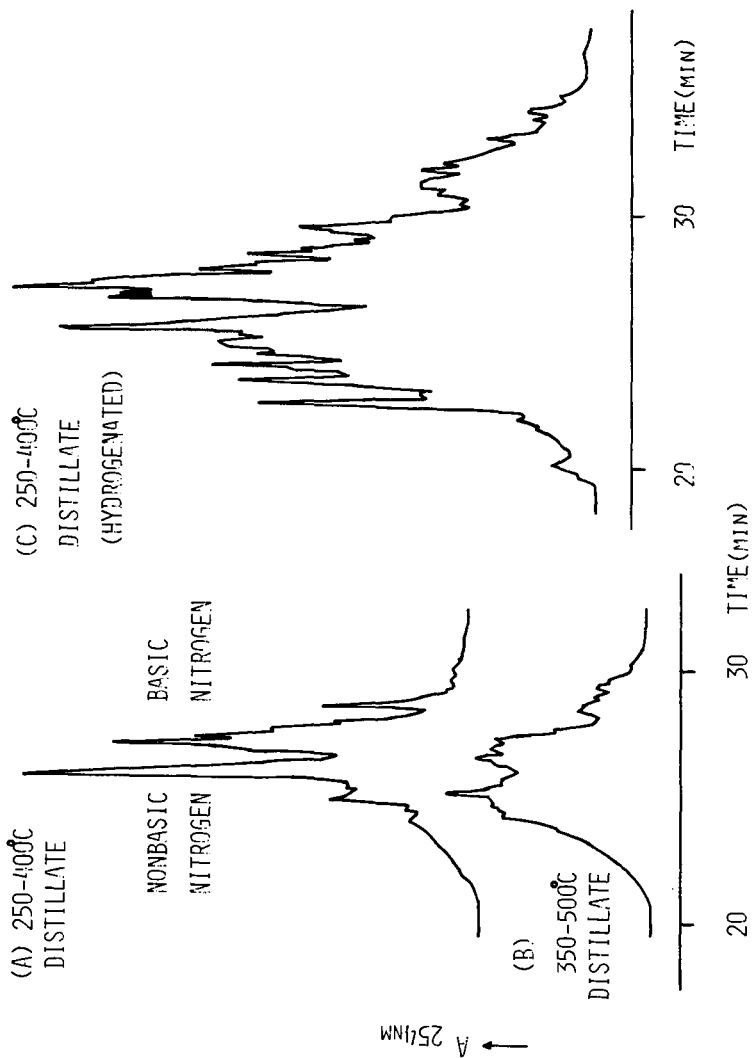


FIGURE 2. CHROMATOGRAMS OF HEAVY PETROLEUM FRACTIONS, (POLAR COMPOUNDS REGION) CONDITIONS AS IN FIGURE 2(B)

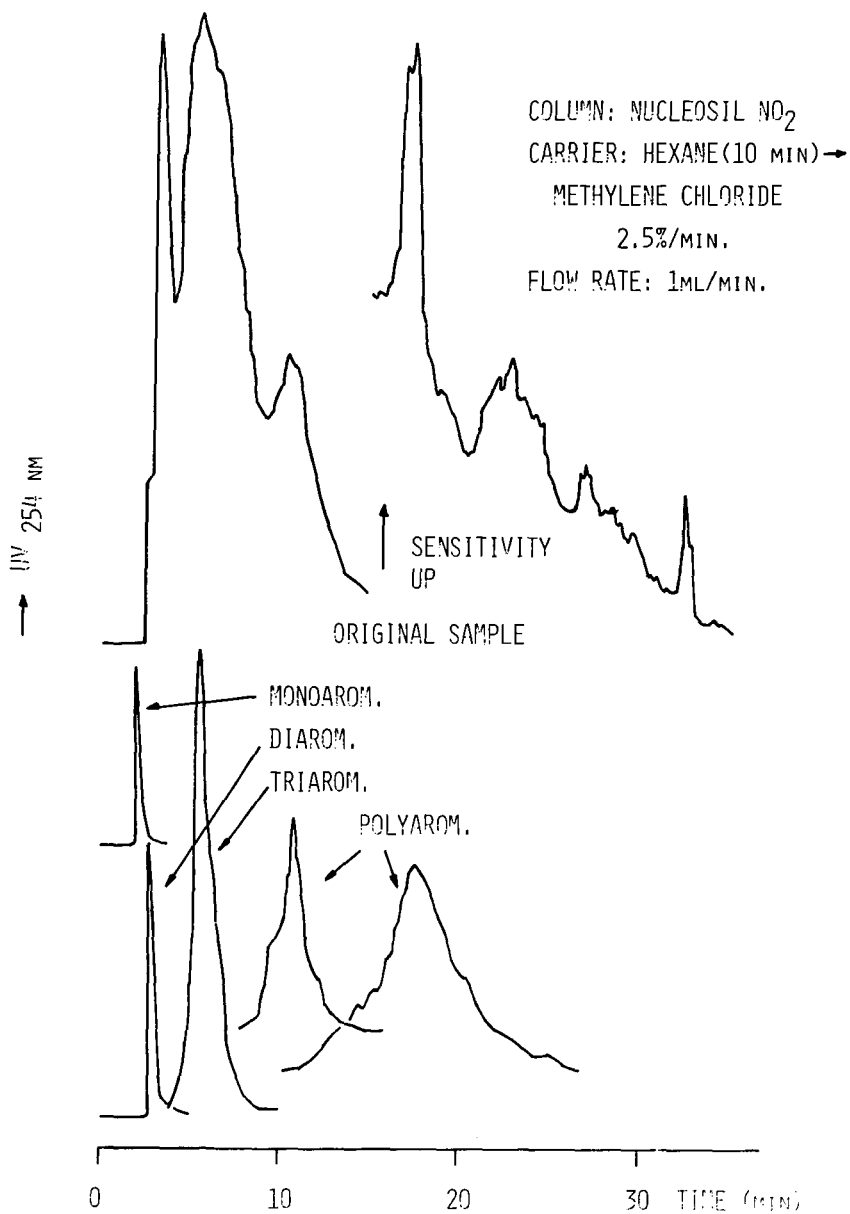


FIGURE 3. CHROMATOGRAMS OF 350-480°C DISTILLATE AND
 ITS SEPARATED FRACTIONS BY ALUMINA CHROMATOGRAPHY